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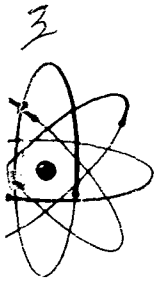

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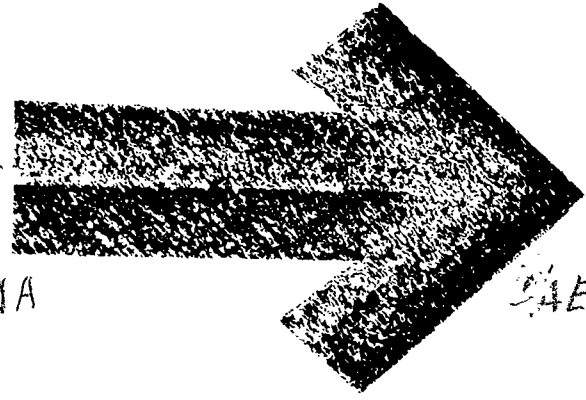

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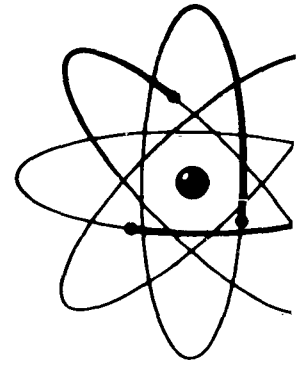

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Constant in HD

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The coupling of nuclear spins by second-order perturbation mechanisms was first proposed and discussed by Ramsey and Purcell[1] in explanation of experimental results obtained by Hahn and Maxwell.[2] Invoking an arbitrary "average energy" denominator to compare magnitudes of the several terms for the HD molecule, Ramsey[3] showed that the dominant contribution to the indirect spin-spin coupling arises from the second-order perturbation theory energy of the Fermi-contact Hamiltonian,[4] $\mathcal{H}_F = (16\pi\beta\hbar/3)\,\Sigma_{k,N}\,\gamma_N\,\delta(\underset{\sim}{r}_{kN})\underset{\sim}{S}_k\cdot\underset{\sim}{I}_N$, where $\underset{\sim}{r}_{kN} = \underset{\sim}{r}_k - \underset{\sim}{r}_N$ and $\underset{\sim}{S}_k$ and $\underset{\sim}{I}_N$ are the electron and nuclear spins respectively. Stephen[5] and others[6] have since performed variational calculations for this same energy.

A new approximate procedure[7] for performing perturbation calculations on simple unperturbed molecular wave-functions introducing no arbitrary parameters, enables the relatively facile calculation of some molecular properties.[8] This procedure is used here to calculate approximately the Fermi-contact contribution, J_F, to the indirect scalar coupling between the nuclear spins in HD. The scalar coupling constant is written as J, where the coupling energy is $E = hJ\underset{\sim}{I}_H\cdot\underset{\sim}{I}_D + h\,\underset{\sim}{I}_H\cdot\underset{\sim}{\mathcal{J}}\cdot\underset{\sim}{I}_D$ and $\underset{\sim}{\mathcal{J}}$ is a traceless tensor whose effect vanishes under the usual experimental conditions. Consider the ground-state described by the Coulson-MO wave-function,[9] $|0(r_1,r_2),0(\sigma_1,\sigma_2)\rangle = 2^{-\frac{1}{2}}N^{-2}\,|(H+D)(1)(H+D)(2)[\alpha(1)\beta(2)-\alpha(2)\beta(1)]\rangle$ assuming the space-and spin-coordinates be separable for the excited states as well. $|H(1)\rangle$ and $|D(1)\rangle$ are one-electron 1s AO's centered on the proton and the deuteron respectively with, e.g. $|H(1)\rangle = (\alpha^3/\pi)^{\frac{1}{2}}\exp(-\alpha\, r_{1H})$, $\alpha = 1.197$, $N^2 = 2(1+\langle A|\,B\rangle)$ and $R_{HD} = 1.4217\ a_o$. J_F can be written, considering both the one-electron and two-electron contributions, as[3]

$$J_F = 2(2/3h)(16\pi\beta\hbar/3)^2\,\gamma_H\,\gamma_D\,\Sigma'(E_o-E_n)^{-1}\Big\{\langle 0,0|\,\delta(\underset{\sim}{r}_{1H})\underset{\sim}{S}_1\,|\,n,n\rangle\cdot\langle n,n|\,\delta(\underset{\sim}{r}_{1D})\underset{\sim}{S}_1\,|\,0,0\rangle + \langle 0,0|\,\delta(\underset{\sim}{r}_{2H})\underset{\sim}{S}_2\,|\,n,n\rangle\cdot\langle n,n|\,\delta(\underset{\sim}{r}_{1D})\underset{\sim}{S}_1\,|\,0,0\rangle\Big\}. \qquad (1)$$

The "covalent approximation" observes[7] that if $\mathcal{H}_o\,|\,0,0\rangle \cong E_o\,|\,0,0\rangle$ ($\cong$ since $|0,0\rangle$ is never an exact eigenfunction of $\mathcal{H}_o$), then $\mathcal{H}_o\,|\,A(1)(A+B)(2),0\rangle \approx E_o\,|\,A(1)(A+B)(2),0\rangle$ and $\mathcal{H}_o\,|B(-)(A+B)(2),0\rangle \approx E_o\,|\,B(1)(A+B)(2),0\rangle$. Let the function $f_N\{\delta(r_{iN'})\}$ for each electron i and nuclei N,N', be defined by the inhomogeneous p.d.e.

$$[f_N\{\delta(\underset{\sim}{r}_{iN'})\},\mathcal{H}_o]\,|\,N(i)\rangle = \delta(\underset{\sim}{r}_{iN'})\,|N(i)\rangle - \langle N(i)|\,\delta(\underset{\sim}{r}_{iN'})\,|N(i)\rangle\,|N(i)\rangle \qquad (2)$$

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The spatial function for electron $j \neq i$ and the spin functions have been suppressed, defining $f\{\delta(\underset{\sim}{r}_i)\}$ to be independent of $\underset{\sim}{r}_j$. For $N = N'$ the solution to Eq. (2) is[10]

$$f_N\{\delta(\underset{\sim}{r}_{iN})\} = (2m/4\pi\hbar^2)(-1/r_{iN} + 2\alpha \ln r_{iN} + 2\alpha r_{iN}) \quad (3)$$

We have not succeeded in solving for $f_N\{\delta(\underset{\sim}{r}_{iN'})\}$, $N \neq N'$, although these f's will be small as the inhomogenities themselves, e.g. $\delta(\underset{\sim}{r}_H)\,|\,D\rangle \sim \exp(-\alpha R_{HD}) = 0.19$, are small. Their contributions are neglected as argued below. Following Dalgarno[11] and Schwartz[10] the commutators of the f's are substituted into Eq.(1) neglecting the non-orthogonality of $|A\rangle$ and $|B\rangle$ with $|n\rangle$ which gives a small error,[7] and the sum over $|n, n\rangle$ is taken, observing that $\langle o|\, \underset{\sim}{S}_i^2\,|\,o\rangle = -\langle o|\, \underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2\,|\,o\rangle = \frac{3}{4}$ and $\langle o|\, \underset{\sim}{S}_i\,|\,o\rangle = 0$. J_F then becomes[12]

$$J_F = h^{-1}(16\pi\beta\hbar/3)^2 \gamma_H \gamma_D N^{-4}\Big\{N^2[\langle (H+D)(1)|\,\delta(\underset{\sim}{r}_{1H}) f_D\{\delta(\underset{\sim}{r}_{1D})\}\,|\,D(1)\rangle + \langle H(1)|\, f_H\{\delta(\underset{\sim}{r}_{1H})\}\delta(\underset{\sim}{r}_{iD})\,|\,H(1)\rangle + X_1] -$$
$$[\langle (H+D(1)(H+D)(2)|\,\delta(\underset{\sim}{r}_{2H}) f_D\{\delta(\underset{\sim}{r}_{1D})\}\,|\,D(1)(H+D)(2)\rangle + \langle (H+D)(1)H(2)|\, f_H\{\delta(\underset{\sim}{r}_{2H})\}\,\delta(\underset{\sim}{r}_{1D})\,|\,H(1)(H+D)(2)\rangle + X_2]\Big\} \quad (4)$$

with X_1 given by $X_1 = \Sigma'(E_o - E_n)^{-1}\langle D(1)(H+D)(2)|\,\delta(\underset{\sim}{r}_{1H})\,|\,n\rangle \langle n|\,\delta(\underset{\sim}{r}_{1D})\,|\,H(1)(H+D)(2)\rangle$ and X_2 analogously. Such terms will clearly be small as both matrix elements involve the value at one nucleus of the AO centered on the other, being of the order of $\exp(-2\alpha R_{HD})$. X_1 and X_2 should each be $\exp(-\alpha R_{HD})$ smaller than the next largest one-electron and two-electron terms respectively, which are themselves $\exp(-\alpha R)$ smaller than the respective dominant terms. The divergence of the Fermi self-coupling ($J_{F,HH}$ or $J_{F,DD}$), when nuclear size corrections are neglected, is observed trivially.

When the necessary integrals are evaluated, the calculated contribution to J_F from the one-electron terms is 3.0 cps while that from the two-electron terms is -32.5 cps for a total of -29.5 cps. The error from both the method and the wave function (e.g., too much ionic contribution) is probably within 25% and will be discussed elsewhere along with results of other calculations. Experiment[13] gives $J_{HD} = 43$ cps of indeterminate sign, and the calculated J_F indicates that indeed J_F is a principal contributor to J_{HD}. (The different orbital contributions[3] will be discussed elsewhere.) The sign of J_{HD} could, in principle, be determined by ultra-high-resolution molecular beam techniques.

The negative calculated J_F is surprising since the approximation using an "average energy" denominator with the usual positive (and arbitrary) ΔE^* gives[3] J_{HD} incorrectly as positive. This exhibits the well-known fallibility[14] of the "average energy" procedure for sums whose numerators are not positive-definite. The negative J_F can be argued physically. Consider the two-electron term, the energy of which is expressed as proportional to $(\underset{\sim}{I}_H \cdot \underset{\sim}{S}_1)(\underset{\sim}{I}_D \cdot \underset{\sim}{S}_2)$ whose dominant contribution has electron 1 on H and electron 2 on D. If H and D have their spins parallel, then by the Pauli principle, either $\underset{\sim}{I}_H \cdot \underset{\sim}{S}_1$ is positive and $\underset{\sim}{I}_D \cdot \underset{\sim}{S}_2$ negative, or <u>vice versa</u>, and the energy which is their product is negative. Since, for the scalar coupling, $E = hJ_{HD}\underset{\sim}{I}_H \cdot \underset{\sim}{I}_D$, J_{HD}

is negative.[15] The quantum mechanical argument would observe that most of the lowest coupled triplet states, rather than being "anti-bonding" states, e.g. $|\mathcal{A}(H-D)(1)(H+D)(2)\rangle$, are "bonding"states of higher AO's, e.g. $|\mathcal{A}(H+D)(1)(H'+D')(2)\rangle$ where H',D' are higher S- states. For such $|n\rangle$ in the (dominant) two-electron sum, whenever the l.h. matrix element is positive, the r.h. one is negative. The product is therefore negative, which with a negative energy denominator and a negative spin matrix element, gives J_{HD} negative.

REFERENCES

1. N. F. Ramsey and E. M. Purcell, Phys. Rev. 85, 143 (1952).

2. E. L. Hahn and D. E. Maxwell, Phys. Rev. 84, 1246 (1951), and 88, 243 (1952). H. G. Gutowsky, D. McCall and C.P. Slichter, Phys. Rev. 84, 589 (1951).

3. N. F. Ramsey, Phys. Rev. 91, 303 (1953).

4. E. Fermi, Z. Physik 60, 320 (1930).

5. M. J. Stephen, Proc. Roy. Soc. A243, 274 (1957).

6. T. P. Das and R. Bersohn, Phys. Rev. 115, 897 (1959); D. E. O'Reilly, J. Chem. Phys. 36, 274 (1962).

7. J. I. Musher, submitted to Ann. Phys. (N.Y.)

8. J. I. Musher, Disc. Faraday Soc. (in press).

9. C. A. Coulson, Trans. Faraday Soc. 33, 1479 (1937).

10. C. Schwartz, Ann. Phys.(N.Y.)2, 156, 170,178 (1959).

11 A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. A233, 70 (1955).

12. This is similar to Eq.(62) of ref. 6, but a different variational function is used for each center analogous to variationally determined screening in simple H_2 wave functions.[9] Calculation shows the important term of Eq.(3) to be the one in r_{iN}. Therefore variational calculations using $r_H|H\rangle^N + r_D|D\rangle$as a trial function would have met with better success than refs. 5 and 6.

13. B. Smaller, E. Yasaitis, E. C. Avery and D. A. Hutchinson, Phys. Rev. 88, 414 (1952); H. Y. Carr and E. M. Purcell, Phys. Rev. 88, 415 (1952).

14. A. D. McLachlan, J. Chem. Phys. 32, 1263 (1960).

15. This should not be looked at, as has been done in the past, from the point of view of additive energies $\underset{\sim}{I}_N \cdot \underset{\sim}{S}_i$, as these are the first-order hf energies which equal to zero when both electrons are included.

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